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DEVELOPMENT OF HIGH-PERFORMANCE TRANSPARENT CONDUCTING OXIDES AND THEIR IMPACT ON THE PERFORMANCE OF CDS/CDTE SOLAR CELLS

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ABSTRACT: This paper begins with a review of the modeled performance of transparent conducting oxides (TCOs) as a function of their free-carrier concentration, mobility, and film thickness. It is shown that it is vital to make a film with high mobility to minimize the width and height of the free-carrier absorption band, and to optimize the optical properties. The free-carrier concentration must be kept sufficiently small that the absorption band does not extend into that part of the spectrum to which the solar cell responds. Despite this consideration, a high electrical conductivity is essential to minimize series resistance losses. Hence, a high mobility is vital for these materials. The fabrication of thin-films of cadmium stannate is then discussed, and their performance is compared with that of tin oxide, both optically and as these materials influence the performance of CdTe solar cells.
Keywords: CdTe - 1: Transparent conducting oxides - 2: Sputtering - 3

1. INTRODUCTION

In recent years we have undertaken both fundamental and applied work on novel transparent conducting oxides (TCOs). The key motivations are that i) almost no new materials have been developed for at least 30 years, and ii) almost all optimized conventional TCOs (virtually irrespective of the method of deposition) give essentially identical optical and electrical properties. We therefore modeled the materials to establish the key parameters influencing their optical and electrical performance, developed high-performance films of cadmium stannate (CTO), and successfully applied these films to CdS/CdTe solar cells. This paper deals with each of these aspects.

2. MODELING

TCOs obey the Drude free-electron model surprisingly well, and our approach was to calculate the optical constants of arbitrary TCOs in terms of their free-carrier concentration, effective mass, and high frequency permittivity. The mobility is also required as an input, and this was calculated as a function of their carrier concentration, using the model of ionized impurity scattering of free- charge developed by Conwell et al. [1]. With this approach, once the effective mass and high-frequency permittivity were specified, the carrier concentration was the only adjustable parameter. This permitted us to calculate the complex permittivity and optical constants. Having calculated the values of refractive index and extinction coefficient, (N and k) we then calculated the transmittance, reflectance and
absorbance of a 500 nm film on glass. The key point to emerge from our modeling was that it is vital to fabricate films with high electron mobility to obtain high optical transmittance the visible part of the spectrum, as well as high electrical conductivity. As we shall show, CTO has a much higher mobility than conventional TCOs.

Figure 1 shows the modeled variation of absorbance with wavelength, the carrier concentration being treated parametrically. The effective mass and high-frequency permittivity were assumed to be 0.35 m_e, and 5, respectively, in accordance with previous observations reported by Dhere et al. [2]. Figure 2 shows the modeled transmittance for the same set of parameters as used in Figure 1. Figure 3 shows the variation of resistivity and mobility, the latter being based on the model of ionized impurity scattering of carriers. The resistivity approaches an asymptotic value of approximately 10^{-4} Ω cm, which, for a 500-nm thick film, is equivalent to 2 Ω/G.

As discussed in the next section, the optical and electrical properties of actual films are very similar to the values predicted by the modeling. It is important to minimize the free-carrier absorbance and simultaneously achieve low resistivity and it is therefore essential to maximize carrier mobility.

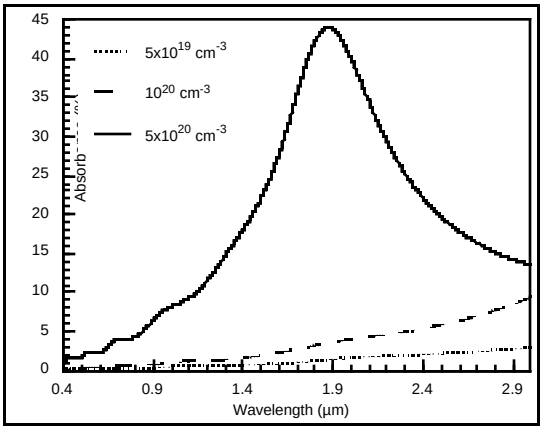

Figure 1:Modeled variation of the free-carrier absorbance of TCO films, the carrier concentration being treated parametrically.

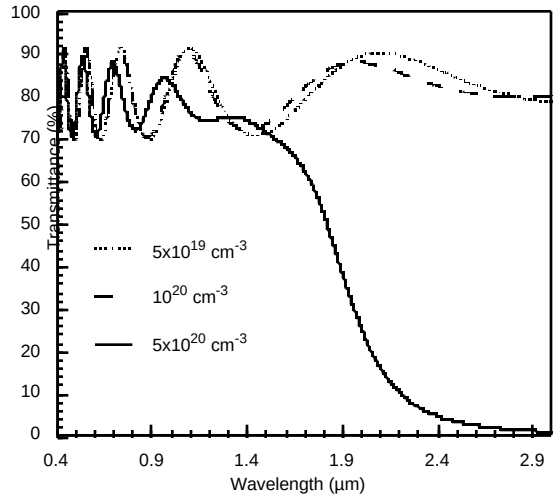

Figure 2: Modeled transmittance of a TCO film: the parameters being the same as in Figure 1.

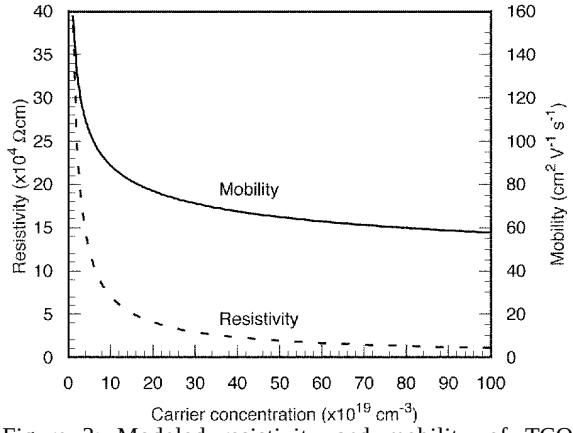

Figure 3: Modeled resistivity and mobility of TCO films.

A previous report by Nozik [3] indicated that high mobility could be achieved in this material, possibly because of a low free-carrier effective mass. There are only two ways to obtain a higher mobility: improve the carrier relaxation time, or use a material with a lower effective mass. The lower limit of resistivity is very similar to values obtained in practice.

Many investigators have published data on TCOs and the most striking feature is the similarity of the optimized electrical and optical properties. This appears to apply to films made from many materials, different deposition techniques, different deposition parameters.

Thus, we originally concluded (a conclusion that was later shown by Mulligan [4] to be incorrect) that the option of improving the relaxation time was probably not realistic. This was the primary motivation for searching for materials with lower effective masses. Careful analysis [5], later showed that the improvement in the properties in general, and the mobility in particular, was in fact due to an improvement in the relaxation time of CTO films, beyond that typically obtained for more traditional materials [2].

Notice that the increasing carrier concentrations in Figure 1 lead to the absorption band gradually extending further into the part of the spectrum to which the solar cells respond. This leads to a reduction of the short-circuit-current density and also causes the TCO film to appear brown. Excessive free-carrier concentration is responsible for the well-known brown appearance of non-optimal TCO films.

3. TCO DEPOSITION AND PERFORMANCE

Films of CTO were deposited by radio-frequency sputtering, in pure oxygen, on room-temperature substrates of soda-lime glass (although higher-quality substrates have also been used). They were then annealed in pure argon, or argon/CdS, at a temperature of up to 680°C. This sequence has previously been shown to give the highest performance films. It has been shown that the structure of films prepared in this way is single-phase spinel but if other processing sequences were used, then multiple phases resulted, which never performed as well as single phase materials. These comments apply to both the conductivity and optical transmittance of the films. When optimized, single-phase films had a resistivity as low as 1.1×10^{-4} Ω cm. A comparison of the optical absorbance of a typical research-quality CTO film and a sample of commercially-available SnO_2, deposited onto a soda-lime substrate, using chemical vapor deposition from a $SnCl_4$ precursor, is shown in Figure 4. The carrier concentrations for the SnO_2 and the CTO were 5×10^{20} cm^{-3} and 3.2×10^{20} cm^{-3}, respectively, and the film thicknesses were about 500 nm for both materials. The mobilities of the films were 15 and 54 $cm^2 V^{-1} s^{-1}$ for the tin oxide and CTO, respectively.

Clearly, the performance of the CTO is considerably superior to that of the tin oxide. The reason for this, in accordance with the modeling data reported above, is the extraordinarily high electron mobility, which was more than 60 $cm^2 V^{-1} s^{-1}$ in some cases.

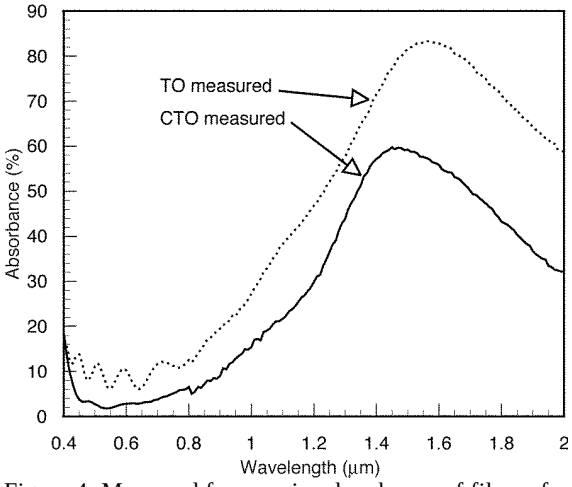

Figure 4: Measured free-carrier absorbance of films of tin oxide and CTO.

Films of CTO were deposited by radio-frequency sputtering, in pure oxygen, on room-temperature substrates of soda glass (although other higher quality substrates have also been used). They were then annealed in pure argon, or argon/CdS, at a temperature of up to 680°C. This sequence has previously been shown to give the highest performance films. It has been shown that the structure of films prepared in this way is single phase spinel but, if other processing sequences were used, the multiple phases resulted. These never performed as well as the single phase materials. These comments apply to both the conductivity and optical transmittance of the films. When optimized, these films had a resistivity as low as $1.1x10^{-4}$ Ω cm. A comparison of the optical absorbance of a typical research-quality CTO film and a sample of commercially-available SnO_2 is shown in Figure 4. The carrier concentrations for the SnO_2 and the CTO were $5x10^{20}$ cm^{-3} and $3.2x10^{20}$ cm^{-3}, respectively, and the film thicknesses were about 0.5 µm for both materials. The mobilities of the films were 15 and 54 cm^2 V^{-1} s^{-1} for the tin oxide and CTO, respectively. Clearly, the performance of the CTO is considerably superior to that of the tin oxide. The reason for this, in accordance with the modeling data reported above, is the extraordinarily high electron mobility, which was more than 60 cm^2 V^{-1} s^{-1} in some cases.

4. APPLICATION OF CADMIUM STANNATE TO CDS/CDTE SOLAR CELLS

The improved material properties of CTO films provide a strong impetus to incorporate them in a superstrate structure. Reduced film resistivity and improved transmittance provide significant device/module design flexibility that did not previously exist. For example, the reduced CTO resistivity permits a thinner front-contact to be used (~200 nm at <10 Ω/sq.), yielding

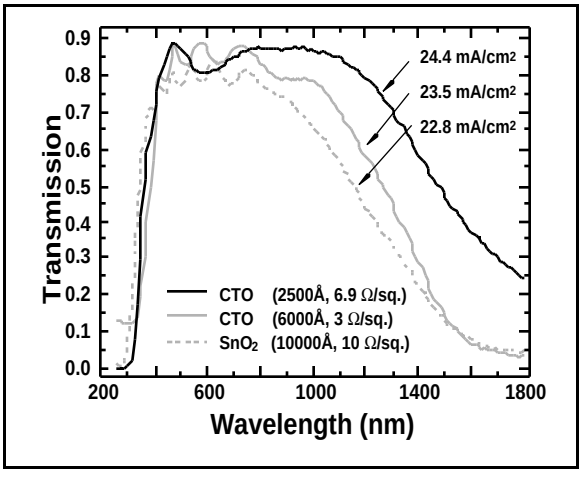

Figure 5: Relationship between J_{sc} and transmittance of tin oxide and CTO films [5].

improved transmission and ultimately improved device performance (by increasing the short-circuit current density, Jsc). Alternatively, a thicker CTO film (~650 nm at ~3 Ω/sq.) could be used that would have the advantage of reducing the number of interconnects required in module production, thereby improving throughput, reducing interconnect losses, and reducing manufacturing costs. Figure 5 shows the relationship between the TCO film transmission and the resulting Jsc for devices deposited on both CTO and SnO_2 superstrates. For example, replacing the 1,000-nm SnO_2 film with a 250-nm CTO film yielded an increase in J_{sc} of more than 1.5 mA/cm^2. It is important to note that devices fabricated on the thicker CTO films always gave the highest fill factors. Fill factors of 75% have been achieved using 600-nm-thick CTO films in ~1-cm^2 square devices. These films have resulted in devices with efficiencies of up to 14.5% (V_{oc}=0.834 V, J_{sc}=23.9 mA/cm^2, FF=72.8%), as measured under standard conditions. Therefore, thicker CTO films, with lower sheet resistivities, may be better suited for module applications. We also find that processing parameters that were optimum for SnO_2-coated glass are not suitable for CTO-coated glass. For example CTO-based devices exhibit optimum performance with significantly lower $CdCl_2$ concentrations than conventional SnO_2-based devices with much better adhesion. Figures 6 and 7 show the current/voltage and relative external quantum-efficiency characteristics of a

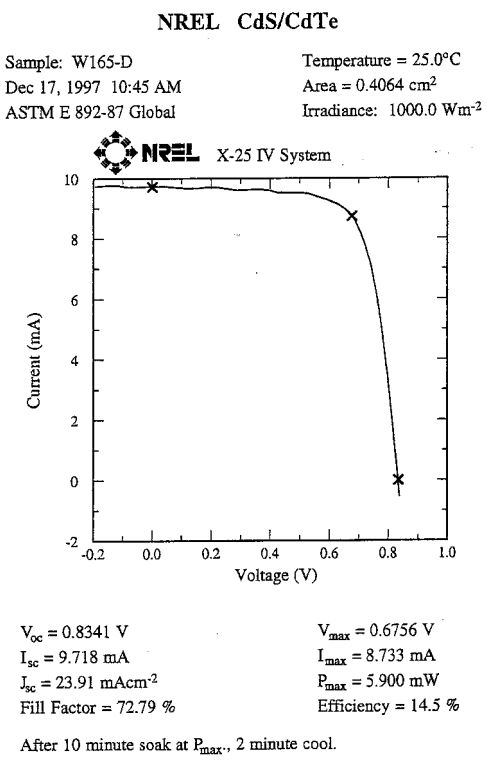

Figure 6: Current/voltage characteristic of a CdS/CdTe device using a CTO top contact.CdS/CdT solar cell with a CTO back-contact.

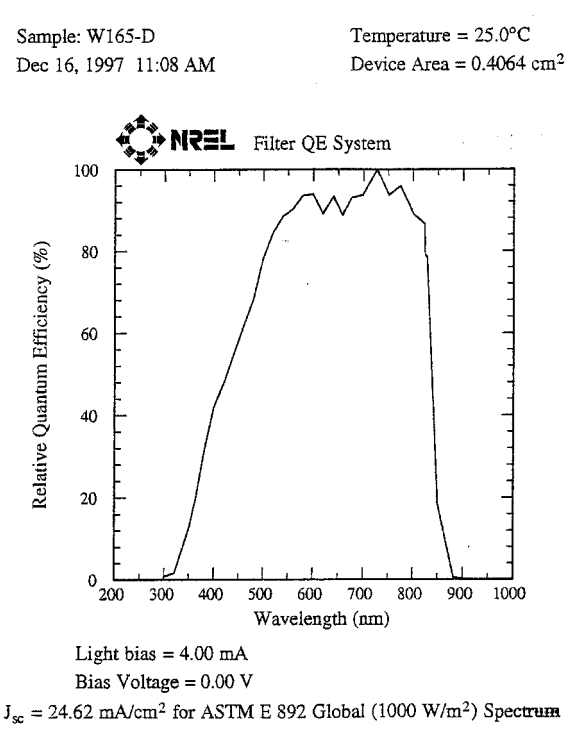

Figure 7: Relative external quantum efficiency of the cell shown in Figure 6.

5. DISCUSSION AND CONCLUSIONS

Modeling shows that a high electron mobility is necessary to obtain TCOs with high transmittance in the visible and high conductivity. Without high mobility, a high carrier concentration is needed to achieve high film conductivity. However, this leads to a severe deterioration of the optical properties of the films and causes browning, with an accompanying reduction in the short-circuit current of the device. In modeling the properties of the TCO films, the dominant scattering mechanism has been assumed to be due to ionized impurities. This is not unreasonable as a first step but has not yet been confirmed unambiguously. This mode of scattering leads to a decreasing mobility with carrier concentration, as shown in Figure 3. However, in previous work, Mulligan [5] and Coutts et al. [6], showed that the mobility actually increases, in some cases, with carrier concentration. This is more difficult to explain, but we suggested that in relatively low-carrier-concentration films, the dominant scattering centers are grain boundaries. As the carrier concentration increases, the material becomes progressively more degenerate, and the Fermi level moves above the peak in the grain-boundary scattering potential. The Fermi electrons (the only ones contributing to the conduction process) are thus unaffected by the grain boundaries. We suggested that at higher carrier concentrations, the dominant scattering centers may change from grain boundaries to ionized impurities and/or acoustic phonons. Hence, we expect to see the mobility of CTO films flatten and eventually decrease at even higher carrier concentrations, if these can be achieved. Hence, there appears to be the possibility that the mobility could be further increased with benefits to the electrical and optical properties.

Annealing of the CTO films in argon, and in close proximity to a CdS film leads to significant increases in both mobility and carrier concentration. The increase in the carrier concentration may cause the increase in the mobility, as suggested above, but the reason for the increase in carrier concentration is not yet understood. Early indications suggest that it may be due to the incorporation of excess cadmium in interstitial donor sites.

CTO is an ideal candidate for superstrate PV devices. Cd_2SnO_4-based CdS/CdTe polycrystalline thin-film solar cells with efficiencies of 14.5% have been prepared for the first time. Although we have not yet achieved a new record efficiency for CdTe cells [7] using CTO back contact window layers, we believe that the performance of these devices is far from optimized.

ACKNOWLEDGEMENTS

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